Effect of Polymeric Additives on the Performances of Polyethersulfone Blend Hollow Fiber Membrane

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Abstract. The article reported the preparation and modification of hydrophobic polyethersulfone (PES) by blending the solution with hydrophilic additives Tetronic 304, Tetronic 704, Tetronic 1307, and Tetronic 908. Polymeric porous membranes are generally prepared by the phase separation of polymer solution. In this work, we prepared hollow fibre membrane by non-solvent induced phase separation (NIPS). Effect of molecular weight of surfactant added on the performance and characteristic of fabricated membrane were investigated. The control PES membrane has the highest contact angle, indicating the lowest hydrophilic. With addition of surfactant Tetronic in the polymer blend hollow fibre membrane, the water contact angle decreased indicates that the membrane surface is more hydrophilic. Scanning electron microscopy (SEM) images for all of the membrane showed the structure of fibre with finger-like macro voids through the cross-section. The sponge-type of structure in the centre path of original membrane was disappearing with addition of Tetronic. Ultrafiltration experiment results showed that water permeability was highest with addition of Tetronic with lowest molecular weight. According to the characteristics of resulting membrane such as hydrophilicity, ultrafiltration performance, and pores structure, surfactant Tetronic was a good additive to produce hydrophilic membrane for drinking water application
Keywords: PES hollow fibre membrane, NIPS, hydrophilic additive, Surfactant Tetronic.

Introduction

One of the most widely polymer used in membrane preparation is polyethersulfone (PES). This polymer is well known in excellent chemical resistance, good thermal stability and mechanical properties. However, hydrophobic property of pure PES was a main disadvantage of this polymer due to fouling problem in the practical application. Many investigations have reported that increasing membrane surface hydrophilicity could effectively inhibit membrane fouling. Hydrophilic modification of membrane surface is one of the methods to minimize protein adsorption and prevent membrane fouling (Wang *et al.*, 2006). Another method well-known to control membrane fouling during application is chemical treatment (Qin *et al.*, 2005). This method is especially useful to solve the problem of irreversible fouling, which is not removed by normal backwash procedure. Various experiments have been done to improve understanding about the effect of this chemical cleaning on the membrane performance.The addition of organic or inorganic components as a third component to a casting solution has been one of the important techniques used in membrane preparation.

The addition of organic and inorganic to the casting solution has been reported as a pore-forming agent and a membrane-modifying agent (Wang *et al.*, 2005; Rahimpour *et al.*, 2007). Polyethersulfone (PES) membrane usually blended with the hydrophilic polymer additive, such as polyvinylpyrrolidone (PVP) and Pluronic F127 in order to improve its hydrophilicity (Jung *et al.*, 2004; Loh *et al.*, 2011). On the other hand, the addition of large amount of hydrophilic polymer additive to the membrane prepared by non-solvent induced phase separation results in decrease of water permeability due to forming sponge layer near the outer and inner surface. Therefore, the addition of polymeric additive into dope solution should be considered based on the properties of main polymer and the third chemical as an additive. The porosity and the pore sizes of the membrane are determine the efficiency of filtration.

In this work, we studied effect of addition of surfactant Tetronic on the morphology of fabricated hollow fibre PES blend membrane. The effect of molecular weight of surfactant Tetronic on the pore structure of membrane was investigated. Four types of selected surfactant Tetronic with difference of molecular weight (Tetronic 304, 704, 908, and 1307) were used in this study. Tetronic in the commercial also available as Poloxamine is a tetra-functional block polymer nonionic surfactant with four polyoxyethylene (POE)-polyoxy-propylene (POP) block joined together by a central ethylene diamine bridge (Moghimi and Hunter, 2000).

Materials and Methods

Material

Polymer PES (Ultrason E6020 P) with average molecular weight 65000 was purchased from BASF Co. N-Methyl-2-pyrrolidone (NMP) as a solvent was obtained from WAKO (Pure Chemical Industries, Ltd, Japan). Surfactant (Tetronic 304; Mw=1650, Tetronic 704; Mw=5500, Tetronic 1307; Mw=18000, and Tetronic 908;Mw=25000) were purchased from BASF Co. Dextran (Mw= 30.000) was purchased from SIGMA (Germany). All the chemicals were used without further purification.

Hollow fiber membrane preparation

Hollow fibre membrane was prepared via non-solvent induced phase separation (NIPS) by a batch-extruder. The conditions of membrane preparation were set up to the constant for all cases as summarized in Table 1. Dope solutions were prepared by dissolving PES and Tetronic in NMP. PES and Tetronic concentration was fixed at 20 and 3wt% respectively. The hollow fibre was extruded from the spinneret and wound on a take-up winder after entering into the coagulation batch to induced phase separation and solidifies the membrane. The polymer flow rate through spinneret was controlled by a gear pump. The spinneret consists of outer and inner tubes and their diameters are 1.00 and 0.70 mm. Water was flow through the inner tube to make lumen of the hollow fibre. The prepared hollow fibre membranes were kept in the pure water before testing.

Table 1 The preparation condition of PES hollow fibre membrane.

Polymer flow rate (m/min)	Water flow rate (m/min)	Take-up speed (m/min)	Air-gap distance (cm)	Temperature (°C)		
				Coagulation bath	Dope vessel	Collecting bath
3.40	12.6	11.2	10	25	25	25

Characterization of Hollow fiber membrane

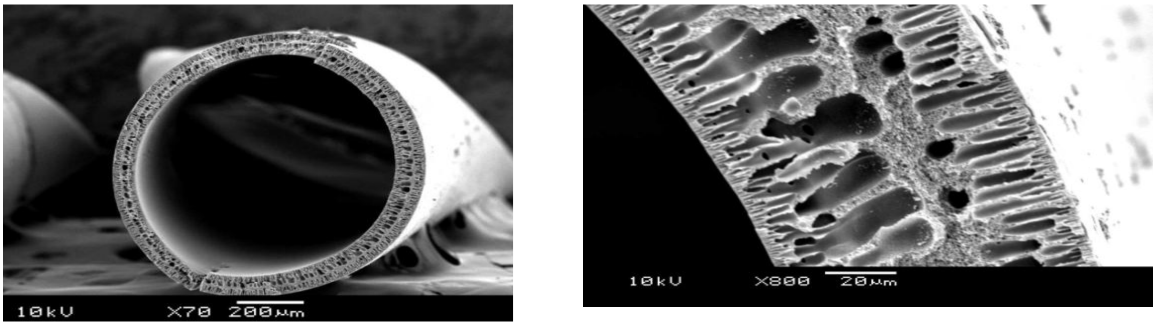
The hollow fibre resulted in this work were characterized for several indicator of membrane properties such as membrane morphology by scanning electron microscopy (SEM), membrane surface roughness by atomic force microscopy (AFM), membrane hydrophilicity by water contact angle measurement, and ultrafiltration performance by single module hollow fibre filtration. For rejection experiment, 1wt% dextran solution was used in this study.

Results and Discussion

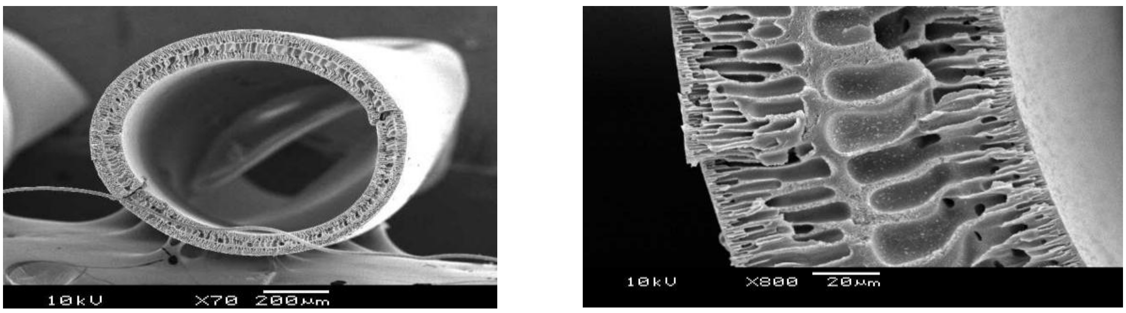
Membrane structures

Membrane morphologies (surface and cross section) were observed by a field emission scanning electron microscope (FE-SEM, JSM-7500F, JEOL Ltd., Japan) with an accelerating voltage of 10 kV. To obtain the dry membrane, the prepared membranes were freeze-dried with a freeze dryer (EYELA, FD-1000, Japan). For the cross section observation, the dry hollow fibre membranes were fractured in liquid nitrogen. The SEM image of whole cross-sections and enlarged cross-sections of original membrane prepared by PES/NMP system and the membrane prepared by PES/NMP/Tetronic 304 (3wt%) system are shown in Figure 1. The similar images of whole cross-section, cross-section enlarged, outer surface, and inner surface of membrane with addition of 3wt% of Tetronic 704, 1307 and 908 were also obtained even though they are not shown here. As shown in Fig.1, in both membranes, the structure of fibre with finger-like macro voids were clearly formed inside the hollow fibre membranes. The number and length of finger-like macro voids was increases with addition of Tetronic 304. The sponge-type of structure in the centre path of original membrane was also disappearing with addition of surfactant Tetronic 304. This finger-like structure in the hollow fibre membrane was attributed by addition of Tetronic in the system. During precipitation process in the coagulation bath, surfactant flow out the membrane (Arahman *et al.*, 2008).

Figure 2 show the morphology of outer surface of PES membrane and PES blend membrane with Tetronic 304 detected by SEM and AFM. A rough structure with small modules is observed by SEM images. The difference between two membrane structures is not so clear because pores are too small to the detected by SEM measurement. Therefore, a Nano structure of both samples were observed by AFM measurement as shown in Figure 2 (b,c). The membrane surface was imaged in a scan area of 1 mm for 10 measurements. Clear nodular structures on the surface of hollow fibre membrane were observed, which are the typical structure of membrane prepared by NIPS method (Wienk *et al.*, 1994; Chung *et al.*, 2002). The averages mean roughness (ra) is 2.42 nm and 4.34 nm for PES, and PES+Tet304, respectively.

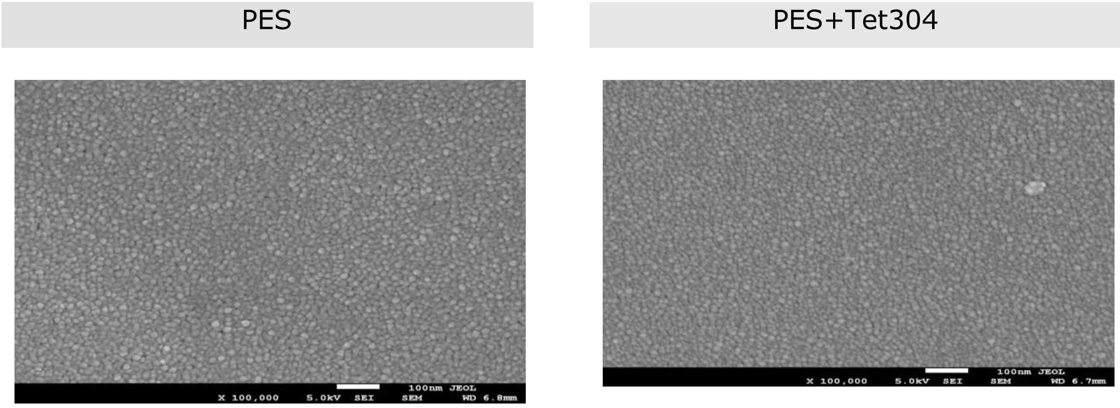


(a). PES

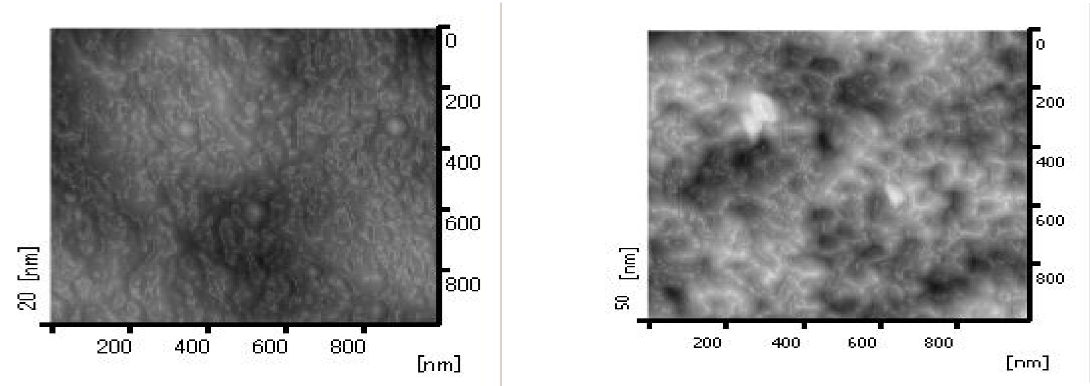


(b). PES+Tet304 (3Wt%)

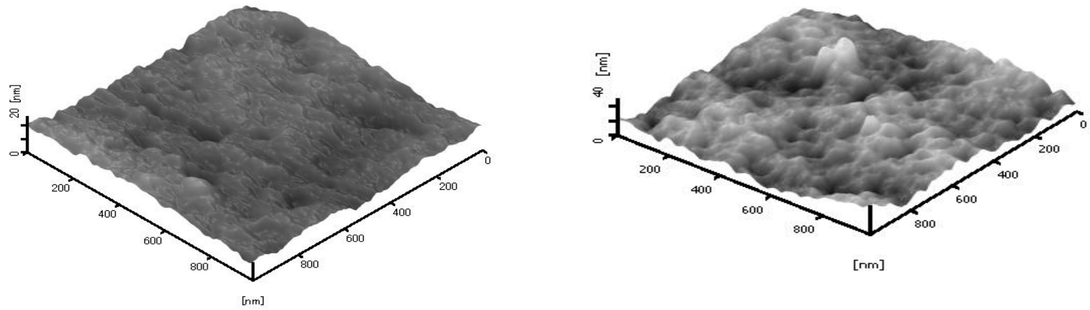
Figure 1. SEM images of whole cross sections and enlarged cross-section PES hollow fiber membrane.



(a). SEM images of outer surface membrane



(b). Two dimensional of AFM images of outer surface membrane.



(c). Three dimensional of AFM images of outer surface membrane.

Figure 2. The morphology of surface PES membrane imaging by SEM and AFM.

Water permeability, solute rejection, and membran hydrophilicity.

Filtration experiments were carried out to study the permeability and solute rejection of PES blend hollow fibre membranes and experiments results were listed in Table 2. As shown in Table 2, when the Tetronic was added in the system, the water permeability increased while solute rejection decreased. The membrane with addition of Tetronic 304 was highest water permeability and the lowest in Dextran rejection. The enhancing of permeation properties was attributed by Tetronic that can be dissolved in water and may act as the pore-forming agent (Arahman *et al.*, 2008; Wang *et al.*, 2005). Table 2 also listed the water contact angle of fabricated membrane. The hydrophilicity properties of the hollow fiber membrane were observed by measuring water contact angle of the outer surface of membrane at room temperature by a contact angle meter (Kyowa Interface Science, CA-A, Japan). Each contact angle was measured for 10 times and an average value was calculated. The original membrane prepared by PES/NMP system was highest water contact angle, indicated low hidrophilicity. The water contact angle were decreased when the system were added Tetronic, indicated the hidrophilicity increases. Increasing molecular weight of surfactant brought about the slight increase of water contact angle.

Table 2. The properties of fabricated hollow fiber membranes

Membrane type	Water Contact Angle (^{O})	Water permeability (L/m^2.hr.atm)	Solute rejection (%)
PES	74	37.4	98.7
PES-Tetronic 304	62	77.7	88.6
PES-Tetronic 704	64	68.9	92.8
PES-Tetronic 1307	63	54.6	95.0
PES-Tetronic 908	66	42.5	94.7

Conclusions

Hydrophilic PES hollow fibre membranes were prepared from PES/NMP solution via non-solvent induced phase separation method. The effect of molecular weight of Tetronic added in the polymer solution on the performance and characteristics of resulting membrane was investigated. Ultrafiltration results with single module showed that the addition of Tetronic was effective to enhance the water permeability of the hollow fibre membranes. Thus, this surfactant could act as one kind of pore-forming agent. Water contact angle observation showed that the hydrophilicity properties of all modified membrane increased. The modified membrane with Tetronic 304 showed the best performance for water permeability. In summary, polymeric surfactant Tetronic was a good additive to produce hydrophilic membrane in order to minimize membrane fouling.

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